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Synthesis of Phosphaguanidines by Hydrophosphination of Carbodiimides with Phosphine Boranes

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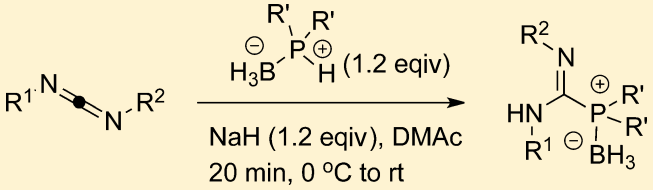
Supporting Information

ABSTRACT: The direct addition of anionic secondary phosphine boranes to carbodiimides yields both chiral and achiral phosphaguanidine boranes under ambient temperature conditions. An analogous preparation of menthol-derived phosphinite boranes is also described. These products can be deborinated to give the corresponding phosphines, and subsequently oxidized to give phosphine oxides. The robustness of this method was further demonstrated in the synthesis of structurally novel cyclic phosphaguanidines.



The preparation of novel phosphines has been facilitated by an increasing number of methods for the hydrophosphonation of carbon−carbon multiple bonds.[1] While many hydrophosphinations exhibit high levels of efficiency and selectivity, most use secondary phosphines that are prone to oxidation or spontaneous combustion. Our research team has taken interest in using phosphine boranes as air-stable, robust alternatives to secondary phosphines in hydrophosphinations.[2] Although other catalytic and thermal stoichiometric hydrophosphinations with phosphine boranes have been reported,[3] we have found that a secondary phosphine borane undergoes a base-mediated hydrophosphination with unactivated alkynes, allenyl phosphine oxides, propargylic alcohols, and propargylic amines.[4] These findings prompted us to further investigate the scope of this straightforward hydrophosphination procedure, and we now report that *N*-alkyl and *N*-aryl carbodiimides, including strained medium ring derivatives, are also competent substrates for this reaction. The resulting phosphaguanidines are of considerable interest as ligands for transition metals and as precursors for metallacycles.[5]

Despite the fact that substoichiometric amounts of alkali-metal bases can effect hydrophosphinations of carbodiimides with secondary phosphines,[5] we opted to utilize our previously optimized conditions for alkyne hydrophosphinations on account of method generality. Accordingly, a dimethylacetamide solution of phosphine borane and carbodiimide (1.2:1 ratio) was sparged with argon to guard against oxidative formation of a phosphinous acid-borane. Treatment of this solution with NaH dispersion, followed by air oxidation of the excess borane phosphide, aqueous workup, and chromatography on SiO_2 afforded the desired phosphaguanidine boranes (Figure 1.)

The reaction was general with regard to carbodiimide substitution, as both aryl and alkyl substituents are tolerated (including commercially available DCC). Electron-rich aryl, electron-poor aryl, and alkyl phosphine boranes are all suitable substrates (**1**−**8**). In addition, both aliphatic and aromatic phosphine boranes can be used for the hydrophosphination (**9**−**15**). For the *P*-dicyclohexyl derivates, a mixture of E_{syn} and Z_{syn} conformers was observed, as previously described for phosphaguanidines.[6] The structures of **4** and **5** were confirmed by X-ray crystal structure analysis. In the solid state, both **4** and **5** assumed the Z_{syn} conformation, as expected.[6] To the best of our knowledge, this is the first general hydrophosphination of carbodiimides with phosphine boranes and represents a versatile alternative to catalytic hydrophosphinations of carbodiimides with secondary phosphines.[7]

After these encouraging preliminary results, we were interested to explore the use of chiral carbodiimides as a means to prepare enantiomerically enriched phosphaguanidines for potential future use of these products as ligands in asymmetric catalysis. Thus, commercially available (*R*)-2-aminoethylbenzene was used to prepare a chiral carbodiimide via the corresponding thiourea. The yields for the subsequent hydrophosphinations were generally comparable to other examples (Figure 1, **9**−**12**, **15**), and since the stereogenic carbons on the amine substituents are unaffected by the

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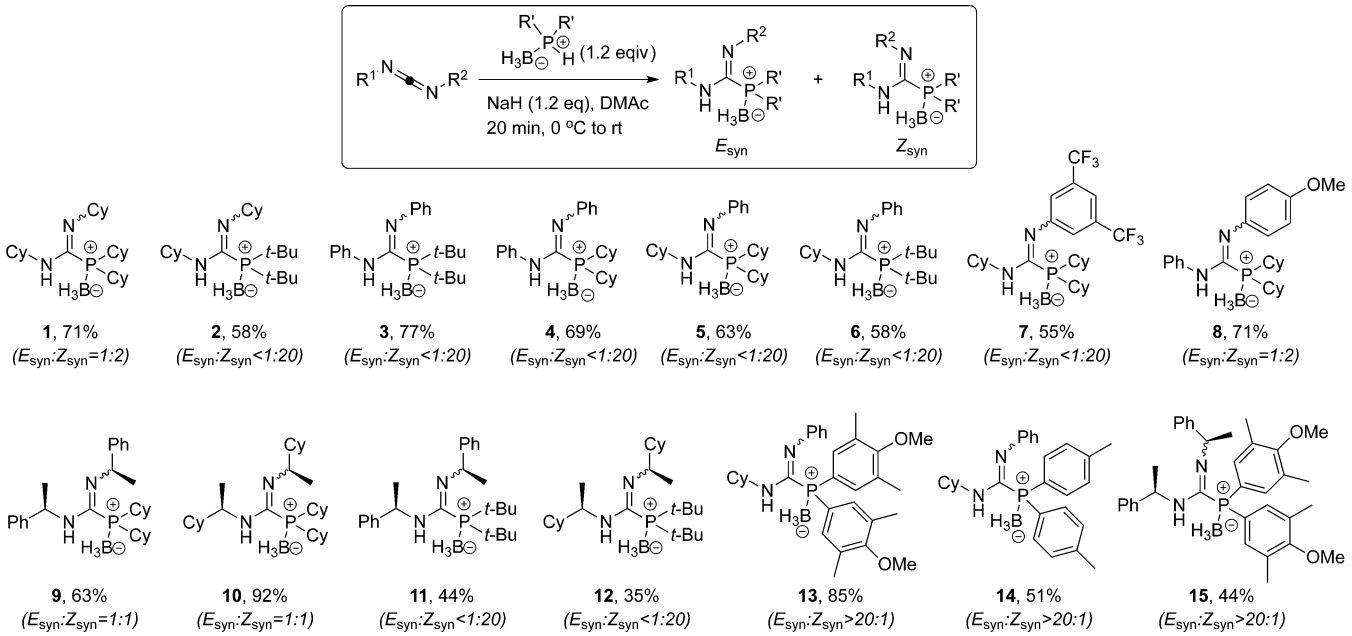


Figure 1. Phosphaguanidine boranes prepared by NaH-mediated hydrophosphination of carbodiimides.

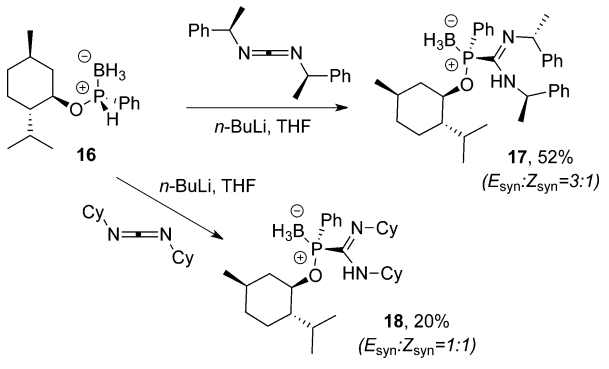
hydrophosphinations, the resulting phosphaguanidine boranes are stereochemically pure.

Another approach toward chiral phosphaguanidines is the use of a chiral phosphine or phosphinite derivative as the hydrophosphination reagent. Menthol-derived phosphinites have previously been used for similar purposes,[8] and **16** was prepared from menthol and $PhPCl_2$, followed by boron complexation (BH_3/THF) and $LiBH_4$ reduction according to a literature procedure.[8]

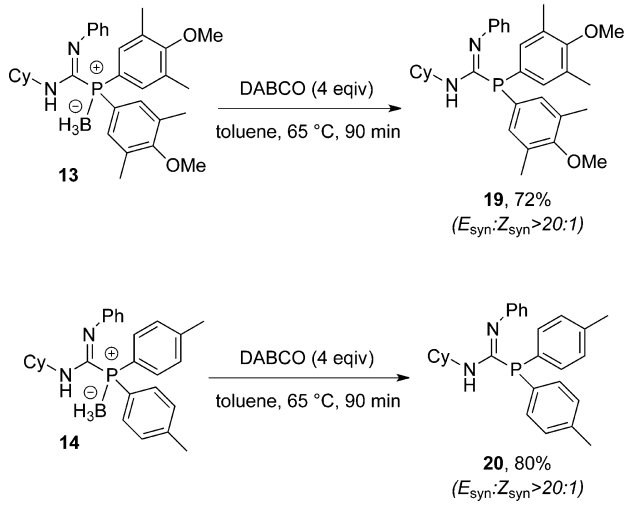
Repeated recrystallizations of a 52:48 R_P:S_P mixture of diastereomers of **16** obtained in 28% yield afforded the R_P diastereomer of **16** as a white crystalline solid.[8] While the carbodiimide hydrophosphination of this substrate with NaH led to significant decomposition, using *n*-BuLi as the base provided **17** and **18** in low to moderate yields (Scheme 1). The hydrophosphination with **16** proceeds with retention of configuration at the phosphorus center.[1g,8,9]

With a general route to both chiral and achiral phosphaguanidines established, we investigated protocols for removing the borane to generate more nucleophilic phosphine reagents and hence potentially more active catalysts. Toward this end, 1,4-diazabicyclo[2.2.2]octane (DABCO) was used for decomplexation at mildly elevated temperature under retention of configuration.[8] These conditions performed well on aromatic phosphine boranes to give phosphaguanidines **19** and **20** (Scheme 2). While the NMR spectra of **19** and **20** were slightly broadened, only one major diastereomer was visible, and in accordance to the literaure data, these compounds were assigned as the E_{syn} isomers.[6] Alcoholysis[10] of phosphane boranes represents an alternative deprotection procedure, but the DABCO method proved to be more general in our hands. We also explored Denmark and Werner's modification of Netherton and Fu's protocol to convert the more sensitive phosphine boranes to their tetrafluoroborate salts.[11] Surprisingly, treatment of **1** with HBF_4 did not cleave the phosphine borane, and the reaction stopped at the *N*-protonated phosphaguanidine tetrafluoroborate salt **21** (Scheme 3). The structure of **21** was secured by X-ray analysis and showed one

Scheme 1. Chiral Phosphinite Boranes Prepared by *n*-BuLi-Mediated Hydrophosphination of Carbodiimides



Scheme 2. P-Deprotection of Phosphine Boranes 13 and 14 to Phosphaguanidines 19 and 20



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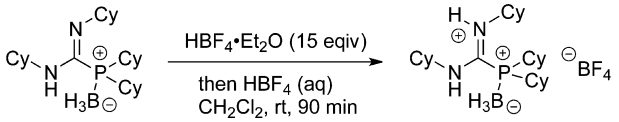
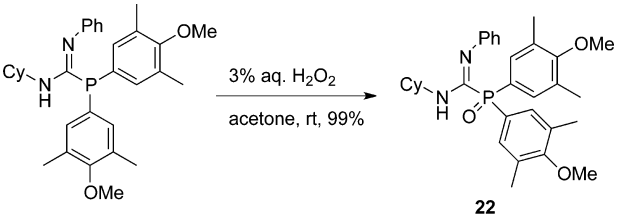
of the cyclohexyl groups positioned *syn* and the second *anti* to the phosphorus atom of the phosphazene.[12]

Scheme 3. Conversion of Phosphaguanidine Borane 1 to the Tetrafluoroborate salt 21



For a proof-of-principle study, conversion of phosphaguanidine **19** to the phosphine oxide **22** was accomplished in nearly quantitative yield by treatment with hydrogen peroxide, while previously reported oxidants such as *t*-butyl hydrogen peroxide and *m*CPBA resulted in the formation of multiple oxidation products (Scheme 4).[12]

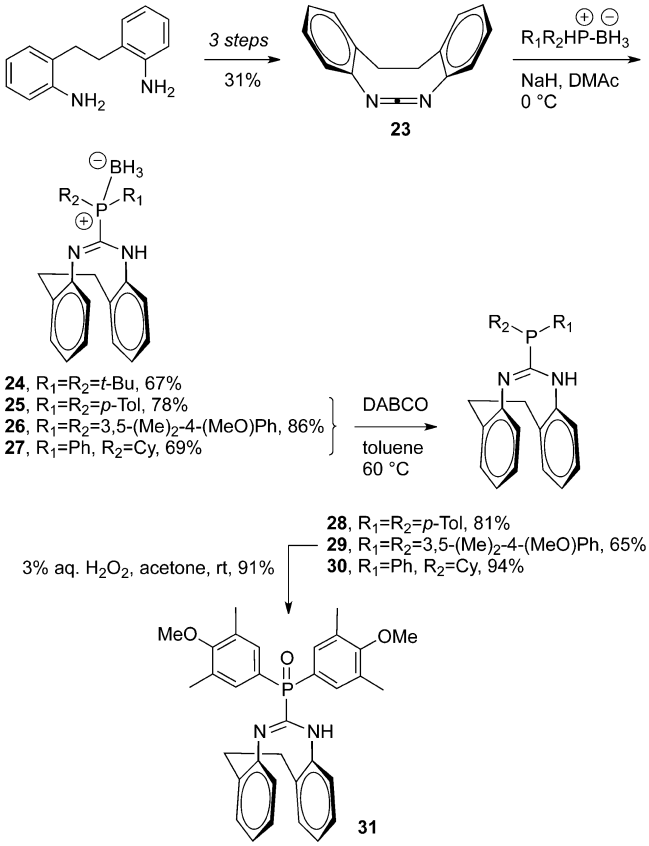
Scheme 4. Formation of Phosphaguanidine Oxide 22



Since some of the phosphaguanidines demonstrated geometric E_{syn}/Z_{syn} isomerism, we sought to restrict the flexibility of the amidine substructure by embedding it into a medium ring system. We also surmised that, in a cyclic phosphaguanidine, the phosphorus atom would be less sterically encumbered and thus more conducive for transition metal or nucleophilic catalysis. Although the requisite cyclic carbodiimides are relatively rare, we were pleased to find that Molina et al. had reported an expedient synthesis of carbodiimide **23** in three steps from a commercially available dianiline (Scheme 5).[13] Hydrophosphination of **23** under standard conditions resulted in phosphaguanidine boranes **24**–**27** in 67–86% yield. Deprotection of **25**–**27** with DABCO provided the corresponding phosphaguanidines **28**–**30** in 65–94% yield, and **29** was further oxidized to phosphine oxide **31** in good yield. A single-crystal X-ray analysis of **24** showed a nearly coplanar alignment of C–N bonds leading to the aromatic rings, with a distance of only 3.04 Å between the two phenyl carbon atoms attached to the phosphaguanidine (Figure 2). Similarly, the ethylene bridge was in an eclipsed conformation with a dihedral angle of 22.0°, forming a compact boatlike nine-membered ring with the guanidine bridge. The juxtaposition of the benzene rings in **24** is reminiscent of a paracyclophane; the distances between opposing carbon atoms vary from 2.8 to 5.1 Å, with an average of 4.0 Å (Figure 2). In comparison, the inter-ring distances in [2,2]paracyclophane and graphite are 3.1 and 3.4 Å, respectively.[14]

In summary, we have developed a straightforward general method for the direct hydrophosphination of carbodiimides with secondary phosphine boranes to afford air-stable phosphaguanidine boranes. For the first time, cyclic phosphaguanidines were prepared by hydrophosphination of a nine-membered cyclic carbodiimide. The borane complexes can be cleaved to afford phosphaguanidines, and in order to demonstrate the feasibility for this transformation, we also generated two phosphaguanidine oxides by oxidation with hydrogen peroxide. Phosphaguanidines and the corresponding *P*-oxides are of potential utility as ligands in transition metal catalysis and organocatalysis.[15]

Scheme 5. Synthesis and P-Deprotection of Cyclic Phosphaguanidines



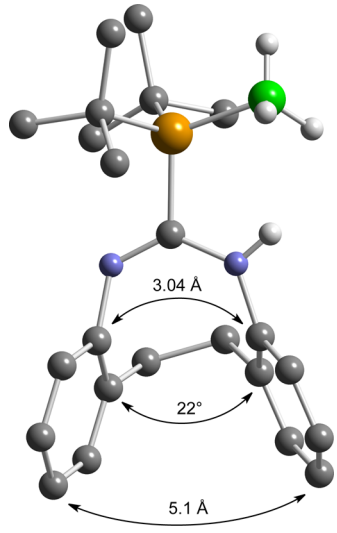


Figure 2. Structure of **24** with selected bond distances and dihedral angles; only the heteroatom–hydrogen bonds are shown.

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EXPERIMENTAL SECTION

General Methods. All reagents were used as received unless stated otherwise. The phosphine boranes utilized herein as well as phenylcyclohexyl thiourea were purchased and used as received. ***Caution!*** *All free secondary phosphines are pyrophoric and they should be handled with care. All of the deprotonations with NaH described below cause gas evolution (H_2) and foaming to various degrees. It is, therefore, best to use a large flask or reactor to contain the foams that are generated.* Accurate mass measurements were performed on a Time-of-Flight mass spectrometer (LC/MSD TOF) operating in a positive electrospray ionization mode with the capillary voltage of 3 kV. The mass spectrometer was tuned and calibrated using a tuning mix prior to sample analysis. Samples were introduced to the mass spectrometer by flow injection using an HPLC system.

General Procedure A: Synthesis of Thioureas from Isothiocyanates. *N-(3,5-Bistrifluoromethyl)phenyl N′-Cyclohexylthiourea (**S1**).*[16] A solution of 3,5-trifluoromethylphenyl isothiocyanate (0.18 mL, 1.0 mmol, 1.0 equiv) and cyclohexylamine (0.12 mL, 1.1 mmol, 1.1 equiv) in CH_2Cl_2 (5 mL) was stirred at rt overnight, resulting in a cloudy solution. The mixture was concentrated and the crude residue was purified by chromatography on SiO_2 (1% MeOH in CH_2Cl_2) to afford **S1** (0.327 g, 0.883 mmol, 88%) as a colorless solid: mp 164.1−165.8 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.34 (s, 2 H), 7.71 (s, 1 H), 4.31−4.27 (m, 1 H), 1.85−1.20 (m, 10 H).

*N-4-Methoxyphenyl N′-Phenylthiourea (**S2**).*[17] Prepared according to General Procedure A from phenyl isothiocyanate (1.128 g, 8.34 mmol) and *p*-anisidine (1.02 g, 8.34 mmol) in CH_2Cl_2 and purified by recrystallization from EtOH/acetone (1:1) to afford **S2** (1.63 g, 6.31 mmol, 76%) as a colorless solid: mp 155.3−156.9 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.94−8.83 (br s, 1 H), 7.58−7.53 (m, 2 H), 7.42−7.32 (m, 4 H), 7.35−7.32 (m, 1 H), 6.94 (t, 2 H, J = 8.7 Hz), 3.82 (s, 3 H).

General Procedure B: Synthesis of Thiourea Starting Materials from Carbon Disulfide. *N,N′-(R)-(+)-Methylbenzylthiourea (**S3**).* ***Caution!*** *STENCH.* To a 500 mL three-neck round-bottom flask were added carbon disulfide (6.62 mL, 110 mmol, 1.00 equiv), EtOH (300 mL), and (*R*)-methylbenzylamine (28 mL, 220 mmol, 2 equiv). The reaction mixture was allowed to stir under reflux (∼88 °C) for 24 h and cooled to ∼5 °C, and the resultant voluminous precipitate was filtered (***Caution!*** *STENCH*). The flilter cake was slurried in 100 mL of hexanes and then refiltered, and the solids were air-dried on the frit for 30 min to afford **S3** (23.1 g, 81.3 mmol, 74%) as colorless needles: mp 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 6 H), 7.13−6.87 (bs, 4 H), 6.07−5.87 (bs, 1 H), 5.12−4.88 (bs, 1 H), 1.47 (d, J = 6.4 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1 (s), 142.3 (s), 128.9 (d), 127.6 (d), 125.7 (d), 54.1 (d), 23.1 (q); HRMS m/z calcd for $C_{17}H_{21}N_2S$ $[M + H]^+$ 285.1420, found 285.1406. The filtrates were deodorized with bleach before disposal.

*N,N′-(R)-(−)-1-Cyclohexylethylthiourea (**S4**).* Prepared according to General Procedure B from carbon disulfide (3.5 mL, 59 mmol, 1.0 equiv), (*R*)-(−)-1-cyclohexylethylamine (15.0 g, 118 mmol, 2.00 equiv), and abs. EtOH (215 mL). The crude material was thoroughly washed with hexanes and subsequently air-dried on the frit for ca. 1 h to give **S4** (9.10 g, 30.7 mmol, 52%) as a colorless, crystalline solid: mp 181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.55 (bs, 1 H), 3.92 (br s, 1 H), 1.81−1.76 (m, 5 H), 1.72−1.65 (m, 4 H), 1.49−1.41 (m, 2 H), 1.29−0.95 (m, 8 H), 1.16 (d, J = 6.5 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.0 (s), 54.6 (d), 43.2 (d), 29.4 (t), 28.9 (t), 26.4 (t), 26.2 (t), 26.1 (t), 17.5 (q); HRMS m/z calcd for $C_{17}H_{33}N_2S$ $[M + H]^+$ 297.2359, found 297.2344. The filtrates were deodorized with bleach before disposal.

General Procedure C: Preparation of Carbodiimides from Thioureas. *N,N′-Diphenylcarbodiimide (**S5**).* To a 100 mL three-neck flask equipped with an inert gas valve were added diphenyl thiourea (1.00 g, 4.38 mmol, 1.00 equiv), Et_3N (1.83 mL, 13.1 mmol, 3.00 equiv), DMAP (0.025 g), and CH_2Cl_2 (45 mL), in the order given. The reaction mixture was cooled to 0 °C, and MsCl (0.678 mL, 114 mmol, 2.00 equiv) was added via syringe over 5 min. The solution was allowed to stir at room temperature for 1 h and concentrated under reduced pressure, and the crude material was filtered through a plug of SiO_2 eluting with CH_2Cl_2. The filtrate was concentrated under reduced pressure and purified by chromatography on SiO_2 (hexanes) under N_2 pressure to afford **S5** (0.700 g, 3.58 mmol, 82%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.30 (m, 4 H), 7.20−7.15 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5 (s), 135.3 (s), 129.5 (d), 125.6 (d), 124.2 (d); HRMS m/z calcd for $C_{13}H_{11}N_2$ $[M + H]^+$ 195.0917, found 195.0903.

*N-Phenyl,N′-cyclohexylcarbodiimide (**S6**).* Prepared according to General Procedure C from *N*-phenyl,*N*-cyclohexylthiourea (3.00 g, 12.8 mmol, 1.00 equiv), DMAP (0.064 g, 0.52 mmol, 4.0 mol %), and Et_3N (5.4 mL, 38.4 mmol, 3.00 equiv) in CH_2Cl_2 (45 mL) and purified by chromatography on SiO_2 under N_2 pressure (20:1 hexanes/EtOAc) to give **S6** (1.21 g, 6.02 mmol, 47%) as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32−7.27 (m, 2 H), 7.14−7.11 (m, 3 H), 3.53−3.45 (m, 1 H), 2.07−2.03 (m, 2 H), 1.83−1.76 (m, 2 H), 1.64−1.25 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9 (s), 136.1 (s), 129.3 (d), 124.5 (d), 123.3 (d), 56.6 (d), 34.9 (t), 26.9 (t), 25.3 (t), 24.3 (t); HRMS m/z calcd for $C_{13}H_{17}N_2$ $[M + H]^+$ 201.1321, found 201.1340.

*N-(3,5-Bistrifluoromethyl)phenyl N′-Cyclohexylcarbodiimide (**S7**).* Prepared according to General Procedure C from thiourea **S1** (0.26 g, 0.71 mmol), triethylamine (0.30 mL, 1.4 mmol, 2.0 equiv), mesyl chloride (0.10 mL, 1.4 mmol, 2.0 equiv), and DMAP (0.004 g, 0.03 mmol, 5 mol %) in CH_2Cl_2 (5 mL) and purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford **S7** (0.197 g, 0.585 mmol, 77%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1 H), 7.46 (s, 2 H), 3.63−3.58 (m, 1 H), 2.03−2.00 (m, 2 H), 1.77 (dd, 2 H, J = 9.6, 4.0 Hz), 1.60−1.49 (m, 3 H), 1.43−1.40 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 133.2, 132.9, 132.5, 132.3, 132.2, 123.4 (q, $^1J_{CF}$ = 271 Hz), 123.2, 117.6 (q, J = 40 Hz), 56.8, 34.7, 25.2, 24.1; HRMS m/z calcd for $C_{15}H_{15}N_2F_6$ $[M + H]^+$ 337.1139, found 337.1141.

*N-4-Methoxyphenyl N′-Phenylcarbodiimide (**S8**).*[18] Prepared according to General Procedure C from thiourea **S2** (1.63 g, 6.31 mmol), triethylamine (2.66 mL, 18.9 mmol, 3.00 equiv), mesyl chloride (0.97 mL, 13 mmol, 2.0 equiv), and DMAP (0.039 g, 0.32 mmol, 5 mol %) in CH_2Cl_2 (60 mL) and purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford **S8** (1.23 g, 5.49 mmol, 87%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.30 (m, 2 H), 7.19−7.13 (m, 5 H), 6.85 (dd, 2 H, J = 6.9, 2.4 Hz), 3.80 (s, 3 H).

*N,N′-(R)-(+)-Methylbenzylcarbodiimide (**S9**).* Prepared according to General Procedure C from thiourea **S3** (2.00 g, 7.03 mmol), DMAP (0.040 g, 0.32 mmol, 5.0 mol %), triethylamine (2.94 mL 21.1 mmol, 3.00 equiv), and mesyl chloride (1.09 mL, 14.1 mmol, 2.00 equiv), in dry CH_2Cl_2 (55 mL) and purified by chromatography on SiO_2 (10% EtOAc/Hex) under N_2 pressure to afford **S9** (1.20 g, 4.78 mmol, 68%, yield adjusted to reflect residual cyclohexane) as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32−7.29 (m, 4 H), 7.26−7.22 (m, 6 H), 4.54 (q, 2 H, J = 7.0 Hz), 1.45 (d, 6 H, J = 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6 (s), 140.3 (s), 128.5 (d), 127.3 (d), 125.9 (d), 56.7 (d), 26.9 (t, C_6H_{12}), 24.6 (q); HRMS m/z calcd for $C_{17}H_{19}N_2$ $[M + H]^+$ 251.1543, found 251.1547.

*N,N′-(R)-(−)-1-Cyclohexylethylcarbodiimide (**S10**).* Prepared according to General Procedure C from thiourea **S4** (5.00 g, 16.9 mmol), DMAP (0.089 g, 0.73 mmol, 4 mol %), triethylamine (7.0 mL, 51, mmol, 3.0 equiv), and mesyl chloride (2.60 mL, 33.8 mmol, 2.0 equiv) in CH_2Cl_2 (175 mL), and purified by chromatography on SiO_2 (20:1 hexanes/EtOAc) to give **S10** (2.13 g, 8.09 mmol, 49%, yield adjusted to reflect residual cyclohexane) as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.21 (pent, 2 H, J = 6 Hz), 1.85−1.79 (m, 2 H), 1.77−1.74 (m, 4 H), 1.69−1.62 (m, 4 H), 1.32−0.93 (m, 12 H), 1.20 (d, 6 H, J = 6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7 (s), 58.3 (d), 44.4 (d), 29.4 (t), 28.9 (t), 26.4 (t), 26.2 (t), 26.1 (t), 19.7 (q); HRMS m/z calcd for $C_{17}H_{31}N_2$ $[M + H]^+$ 263.2482, found 263.2464.

General Procedure D: Hydrophosphination of Carbodiimides. *(N,N′-Dicyclohexylcarbamimidoyl)-dicyclohexylphosphine Borane (**1**).* A 100 mL three-neck flask equipped with a direct Ar line, inert gas valve, and septum was charged with DCC (1.00 g, 4.85 mmol), dicyclohexylphosphine borane (1.03 g, 4.85 mmol, 1.00 equiv), and dry dimethylacetamide (12 mL), in that order. Argon was

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sparged through the reaction mixture for 10 min, and then the flask was placed in an ice bath and cooled to ca. 2 °C. NaH dispersion (0.193 g, 4.85 mmol, 1.00 equiv, 60%) was added, causing immediate gas evolution and foaming, and giving a colorless solution. After 15 min, the ice bath was removed and the mixture was allowed to warm to rt for 35 min. The reaction mixture was then poured into 5 M NH_4Cl (50 mL) and extracted with methyl *t*-butyl ether (2 × 50 mL). The combined organic extracts were washed with H_2O (1 × 100 mL) and dried ($MgSO_4$), and the solvents were removed in vacuo to give a colorless solid that was recrystallized from EtOAc (3 mL) to give **1** (1.67 g, 3.98 mmol, 71%) as a colorless ca. 1:2 mixture of E_{syn} and Z_{syn} conformers: mp 131 °C; ^{1}H NMR (500 MHz, C_6D_6) δ 5.86 (br s, 0.3 H), 5.65−5.60 (m, 0.7 H), 4.07 (br s, 0.3 H), 3.59−3.50 (m, 1 H), 3.47−3.38 (m, 0.7 H), 2.22−2.12 (m, 2 H), 2.02−0.95 (m, 45 H), 0.6−0.15 (m, 2 H); ^{13}C NMR (125 MHz, C_6D_6) δ 145.9 (s, $^1J_{CP}$ = 83 Hz), 143.1 (s, $^1J_{CP}$ = 24 Hz), 59.4 (d, $^3J_{CP}$ = 8 Hz), 57.6 (d, $^3J_{CP}$ = 12 Hz), 54.5 (d, $^3J_{CP}$ = 7 Hz), 50.3 (d, $^3J_{CP}$ = 6 Hz), 36.4 (t), 36.0 (d), 35.7 (d), 35.7 (t), 35.2 (t), 33.2 (d), 32.9 (d), 32.6, 29.2, 28.8, 27.6, 27.55, 27.53, 27.52, 27.49, 27.46, 27.44, 27.4, 27.02, 27.00, 26.87, 26.86, 26.8, 26.7, 26.6, 26.32, 26.31, 26.0, 25.4, 25.1; ^{31}P NMR (202 MHz, C_6D_6) δ 50.9; HRMS *m*/*z* calcd for $C_{25}H_{49}BN_2P$ $[M + H]^+$ 419.3721, found 419.3707.

*(N,N′-Dicyclohexylcarbamimidoyl)-di-tert-butylphosphine Borane (**2**).* Prepared according to General Procedure D from DCC (1.00 g, 4.84 mmol), di-*t*-butyl phosphine borane (0.931 g, 5.82 mmol, 1.20 equiv), and NaH (0.233 g, 5.82 mmol, 1.20 equiv, 60%) in DMAc (12 mL) to afford **2** (1.02 g, 2.77 mmol, 58%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65−5.60 (m, 1 H), 3.53−3.47 (m, 1 H), 3.39−3.30 (m, 1 H), 1.93−1.85 (m, 2 H), 1.80−1.70 (m, 6 H), 1.65−1.50 (m, 3 H), 1.40−1.20 (m, 27 H), 0.90−0.20 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4 (s, $^1J_{CP}$ = 83 Hz), 57.6 (d, $^3J_{CP}$ = 12 Hz), 54.0 (d, $^3J_{CP}$ = 8 Hz), 34.9 (t), 34.6 (t), 33.5 (s, $^1J_{CP}$ = 27 Hz), 28.3 (q, $^2J_{CP}$ = 2 Hz), 26.9 (t), 26.0 (t), 25.5 (t), 24.8 (t), 24.6 (t); ^{31}P NMR (202 MHz, $CDCl_3$) δ 49.6; HRMS *m*/*z* calcd for $C_{21}H_{45}BN_2P$ $[M + H]^+$ 367.3408, found 367.3411.

*(N,N′-Diphenylcarbamimidoyl)-di-tert-butylphosphine Borane (**3**).* Prepared according to General Procedure D from **S5** (0.380 g, 1.96 mmol), di-*t*-butyl phosphine borane (0.376 g, 2.35 mmol, 1.20 equiv), and NaH (0.094 g, 2.4 mmol, 1.2 equiv, 60%) in DMAc (5 mL) and purified by recrystallization from cyclohexane to afford **3** (0.530 g, 1.49 mmol, 77%) as a colorless solid: mp 94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (br s, 1 H), 6.95 (q, *J* = 8 Hz, 4 H), 6.84 (t, *J* = 7 Hz, 1 H), 6.74 (t, *J* = 7 Hz, 1 H), 6.64−6.61 (m, 4 H), 1.56 (s, 9 H), 1.54 (s, 9 H), 0.76 (br q, $^1J_{HB}$ = 85 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0 (s, $^3J_{CP}$ = 12 Hz), 146.1 (s, $^1J_{CP}$ = 76 Hz), 137.7 (s, $^3J_{CP}$ = 8 Hz), 128.00 (d), 127.96 (d), 123.9 (d), 122.4 (d), 121.9 (d), 120.3 (d), 34.2 (s, $^1J_{CP}$ = 26 Hz), 28.4 (q, $^2J_{CP}$ = 2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 52.0; HRMS *m*/*z* calcd for $C_{21}H_{33}BN_2P$ $[M + H]^+$ 355.2469, found 355.2465.

*(N,N′-Diphenylcarbamimidoyl)-dicyclohexylphosphine Borane (**4**).* Prepared according to General Procedure D from **S5** (0.300 g, 1.60 mmol), dicyclohexyl phosphine borane (0.395 g, 1.90 mmol, 1.19 equiv), and NaH (0.124 g, 1.90 mmol, 1.19 equiv, 60%) in DMAc (3.86 mL) and purified by recrystallization from hexanes to afford **4** (0.45 g, 1.1 mmol, 69%) as a colorless solid: mp 99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1 H), 7.10−6.70 (m, 8 H), 6.62 (d, *J* = 7.5 Hz, 2 H), 2.25−2.10 (m, 2 H), 1.95−1.60 (12 H), 1.55−1.40 (m, 3 H), 1.40−1.20 (m, 5 H), 0.60 (br q, $^1J_{HB}$ = 85 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4 (d, $^3J_{CP}$ = 10 Hz), 145.1 (d, $^1J_{CP}$ = 67 Hz), 138.1 (s), 128.2 (d, J_{CP} = 6 Hz), 124.0 (s), 122.6 (d), 121.6 (d), 120.4 (d), 34.5 (d, $^1J_{CP}$ = 38 Hz), 32.4 (d, $^1J_{CP}$ = 31 Hz), 27.0, 26.8, 26.62, 26.58, 26.53, 26.46, 26.40, 26.36, 26.32, 25.88, 25.87, 25.65, 25.64, 24.76, 24.73; ^{31}P NMR (202 MHz, $CDCl_3$) δ 40.7. A single crystal suitable for X-ray analysis was grown from cyclohexane. The X-ray crystal structure data for this compound have been deposited (CCDC No. 997591).

*(N-Cyclohexyl,N′-phenylcarbamimidoyl)-dicyclohexylphosphine Borane (**5**).* Prepared according to General Procedure D from **S6** (0.500 g, 2.50 mmol), dicyclohexyl phosphine borane (0.637 g, 3.00 mmol, 1.20 equiv), and NaH (0.120 g, 3.00 mmol, 1.20 equiv, 60%) in DMAc (5 mL) and purified by trituration with cyclohexane to afford **5** (0.650 g, 1.58 mmol, 63%) as a colorless solid: mp 93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.24 (m, 2 H), 7.00 (t, *J* = 7 Hz, 1 H), 6.81 (d, *J* = 7 Hz, 2 H), 5.69 (br s, 1 H), 3.01 (br s, 1 H), 2.20−2.10 (m, 2 H), 1.91−1.76 (m, 8 H), 1.78−1.38 (m, 11 H), 1.34−1.20 (m, 6 H), 1.09−0.95 (m, 3 H), 0.93−0.80 (m, 2 H), 0.46 (br q, $^1J_{HB}$ = 67 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6 (s, $^3J_{CP}$ = 14 Hz), 146.7 (s, $^1J_{CP}$ = 70 Hz), 128.6 (d), 122.1 (d), 120.3 (d), 51.7 (d), 33.24 (d), 32.1 (d, $^1J_{CP}$ = 34 Hz), 26.9, 26.73, 26.70, 26.64, 26.61, 26.5, 26.02, 26.01, 25.3, 24.3; ^{31}P NMR (202 MHz, $CDCl_3$) δ 39.2; HRMS *m*/*z* calcd for $C_{25}H_{43}BN_2P$ $[M + H]^+$ 413.3251, found 413.3231. A single crystal suitable for X-ray analysis was grown from cyclohexane. The X-ray crystal structure data for this compound have been deposited (CCDC No. 997592).

*(N-Cyclohexyl,N′-phenylcarbamimidoyl)-di-tert-butylphosphine Borane (**6**).* Prepared according to General Procedure D from **S6** (0.380 g, 1.89 mmol), di-*t*-butyl phosphine borane (0.363 g, 2.27 mmol, 1.20 equiv), and NaH (0.091 g, 3.00 mmol, 1.59 equiv, 60%) in DMAc (5 mL) and purified by chromatography on SiO_2 (hexanes) to afford **6** (0.432 g, 1.20 mmol, 58%) as a yellow oil that crystallized on standing: mp 99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8 Hz, 2 H), 6.94 (t, *J* = 7 Hz, 1 H), 6.80 (d, *J* = 7.5 Hz, 2 H), 6.04 (br s, 1 H), 2.89−2.80 (m, 1 H), 1.65−1.25 (m, 22 H), 1.10−0.95 (m, 3 H), 0.90−0.75 (m, 3 H), 0.58 (br q, $^1J_{HB}$ = 80 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5 (s, $^3J_{CP}$ = 13 Hz), 147.3 (s, $^1J_{CP}$ = 77 Hz), 128.5 (d), 121.7 (d), 119.8 (d, $^4J_{CP}$ = 1 Hz), 52.0 (d, $^3J_{CP}$ = 6 Hz), 33.8 (d, $^1J_{CP}$ = 26 Hz), 33.3, 31.6, 30.9, 28.9 (J_{CP} = 2 Hz), 28.3 (q, $^2J_{CP}$ = 2 Hz), 28.2 (J_{CP} = 2 Hz), 26.9, 25.3, 24.3, 22.7, 14.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ 51.4 ($^1J_{PB}$ = 40 Hz); HRMS *m*/*z* calcd for $C_{21}H_{39}BN_2P$ $[M + H]^+$ 361.2938, found 361.2920.

*(N-Cyclohexyl,N′-(3,5-trifluoromethyl)phenylcarbamimidoyl)-dicyclohexylphosphine Borane (**7**).* Prepared according to General Procedure D from **S7** (0.106 g, 0.315 mmol), dicyclohexyl phosphine borane (0.080 g, 0.38 mmol, 1.20 equiv), and NaH (0.015 g, 0.38 mmol, 1.21 equiv, 60%) in DMAc (1.5 mL) and purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford **7** (0.095 g, 0.17 mmol, 55%) as a clear oil that solidified to a colorless solid on standing: mp 97.5−98.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (t, 1 H, *J* = 9.2 Hz), 6.30 (d, 2 H, *J* = 6.8 Hz), 5.84 (br s, 1 H), 3.07 (br s, 1 H), 2.10−2.00 (m, 2 H), 1.90−0.75 (m, 36 H); ^{13}C NMR (100 MHz, $CDCl_3$, CF_3 not resolved) δ 164.5, 164.3, 162.0, 161.9, 153.2, 147.9 (d, $^1J_{CP}$ = 68 Hz), 103.5 (d, $^3J_{CP}$ = 25 Hz), 97.2 (t, $^3J_{CP}$ = 27 Hz), 52.0, 33.1, 32.3, 31.9, 26.9, 26.7, 26.7, 25.9, 25.2, 24.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ −44; HRMS *m*/*z* calcd for $C_{27}H_{38}F_6N_2P$ $[M + H - BH_3]^+$ 535.2677, found 535.2661.

*(N-Phenyl,N′-4-methoxyphenylcarbamimidoyl)-dicyclohexylphosphine Borane (**8**).* Prepared according to General Procedure D from **S8** (0.200 g, 0.892 mmol), dicyclohexyl phosphine borane (0.227 g, 1.07 mmol, 1.20 equiv), and NaH (0.043 g, 1.1 mmol, 1.20 equiv, 60%) in DMAc (2 mL) and purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford **8** (0.275 g, 0.630 mmol, 71%) as an oily ca. 1:2 mixture of E_{syn} and Z_{syn} conformers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.48 (m, 1 H), 7.00−6.50 (m, 9 H), 3.67 (s, 3 H), 2.30−2.10 (m, 2 H), 1.95−1.20 (m, 20 H), 0.90−0.20 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.5 (s), 155.5 (s), 148.5 (s, J_{CP} = 9 Hz), 145.2 (s, $^1J_{CP}$ = 70 Hz), 144.6 (s, $^1J_{CP}$ = 38 Hz), 141.7 (J_{CP} = 11 Hz), 131.3 (J_{CP} = 6 Hz), 128.1, 123.9, 123.8, 122.3, 121.6, 120.5, 113.6, 113.4, 55.6 (q), 55.5 (q), 34.7, 34.5, 32.6, 32.2, 31.6, 29.1, 27.0, 26.8, 26.7, 26.62, 26.58, 26.0, 25.3, 22.7, 20.7, 14.1, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ −43; HRMS *m*/*z* calcd for $C_{26}H_{36}N_2OP$ $[M + H - BH_3]^+$ 423.2565, found 423.2534.

*(N,N′-(R)-(+)-Methylbenzylcarbamimidoyl)-dicyclohexylphosphine Borane (**9**).* Prepared according to General Procedure D from **S9** (0.500 g, 2.00 mmol), dicyclohexyl phosphine borane (0.445 g, 2.10 mmol, 1.05 equiv), and NaH (0.084 g, 2.1 mmol, 1.1 equiv, 60%) in DMAc (5 mL) and purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford **9** (0.587 g, 1.27 mmol, 63%) as an an oily ca. 1:1 mixture of E_{syn} and Z_{syn} conformers that partially crystallized on standing: $[\alpha]_D$ +53.2 (*c* 0.172, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40−7.19 (m, 8 H), 7.05−7.00 (m, 1.5 H), 6.79−6.75 (m, 1 H),

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6.07−6.02 (m, 0.5 H), 5.70−5.63 (m, 0.5 H), 5.04 (pent, J = 7 Hz, 0.5 H), 4.75−4.63 (m, 1.5 H), 2.32−0.86 (m, 22 H), 1.46 (d, J = 7 Hz, 1.5 H), 1.36 (d, J = 6 Hz, 1.5 H), 1.31 (d, J = 7 Hz, 1.5 H), 1.04 (d, J = 6 Hz, 1.5 H), 0.9−0.2 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5 (s, J_{CP} = 1 Hz), 146.8 (s, J_{CP} = 1 Hz), 145.8 (s, $^1J_{CP}$ = 84 Hz), 145.4 (s, $^1J_{CP}$ = 90 Hz), 143.3 (s), 143.1 (s), 128.7 (d), 128.3 (d), 128.2 (d), 127.9 (d), 127.1 (d), 126.44 (d), 126.39 (d), 126.2 (d), 126.0 (d), 125.9 (d), 125.5 (d), 125.3 (d), 58.5 (d, $^3J_{CP}$ = 7 Hz), 57.1 (d, $^3J_{CP}$ = 12 Hz), 54.8 (d, $^3J_{CP}$ = 8 Hz), 51.8 (d, $^3J_{CP}$ = 6 Hz), 34.9 (d, $^1J_{CP}$ = 28 Hz), 34.5 (d, $^1J_{CP}$ = 29 Hz), 32.5 (d, $^1J_{CP}$ = 23 Hz), 32.2 (d, $^1J_{CP}$ = 28 Hz), 28.7 (t), 28.1 (t), 28.0 (t), 27.8 (q), 27.4 (t), 26.89 (t), 26.85 (t), 26.80 (t), 26.78 (t), 26.75 (t), 26.71 (t), 26.69 (t), 26.66 (t), 26.61 (t), 26.6 (t), 26.5 (t), 26.32 (t), 26.31 (t), 26.20 (t), 26.18 (t), 26.14 (t), 26.10 (t), 26.02 (q), 25.97 (t), 25.95 (t), 25.67 (t), 25.65 (t), 25.4 (t), 25.3 (t), 25.25 (t), 25.24 (t), 23.0 (q); ^{31}P NMR (202 MHz, $CDCl_3$) δ 37.9, 36.9; HRMS m/z calcd for $C_{29}H_{45}BN_2P$ $[M + H]^+$ 463.3408, found 463.3441.

*(N,N′-(R)-(−)-1-Cyclohexylethylcarbamimidoyl)-dicyclohexylphosphine Borane (**10**).* Prepared according to General Procedure D from **S10** (0.800 g, 3.04 mmol), dicyclohexyl phosphine borane (0.776 g, 3.66 mmol, 1.20 equiv), and NaH (0.146 g, 3.66 mmol, 1.20 equiv, 60%) in dimethylacetamide (7 mL) and purified by chromatography on SiO_2 (hexanes) to afford **10** (1.33 g, 2.80 mmol, 92%) as a yellow oily ca. 1:1 mixture of E_{syn} and Z_{syn} conformers that formed a crystalline solid on standing: $[\alpha]_D$ −59.6 (c 0.225, CH_2Cl_2); mp 82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20−5.13 (m, 1 H), 3.48−3.36 (m, 2 H), 2.17−1.50 (m, 28 H), 1.37−1.09 (m, 16 H), 1.06 (d, J = 6 Hz, 3 H), 1.01 (d, J = 6 Hz, 3H), 0.38 (br q, $^1J_{HB}$ = 78 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7 (s, $^1J_{CP}$ = 88 Hz), 57.4 (d, $^3J_{CP}$ = 13 Hz), 55.0 (d, $^3J_{CP}$ = 8 Hz), 45.5 (d), 43.9 (d), 32.4 (d, $^1J_{CP}$ = 35 Hz), 32.1 (d, $^1J_{CP}$ = 35 Hz), 30.2, 29.2, 29.0 (J_{CP} = 4 Hz), 26.9, 26.8, 26.7, 26.6, 26.5, 26.4, 26.3, 26.2, 26.1, 25.9, 19.8 (q), 18.68 (q), 18.67 (q); ^{31}P NMR (202 MHz, $CDCl_3$) δ 37.4; HRMS m/z calcd for $C_{29}H_{57}BN_2P$ $[M + H]^+$ 475.4347, found 475.4324.

*(N,N′-(R)-(+)-Methylbenzylcarbamimidoyl)-di-tert-butylphosphine Borane (**11**).* Prepared according to General Procedure D from **S9** (0.500 g, 2.00 mmol), di-*tert*-butyl phosphine borane (0.384 g, 2.40 mmol, 1.20 equiv), and NaH (0.096 g, 2.4 mmol) in DMAc (5.0 mL) and purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford **11** (0.361 g, 0.880 mmol, 44%) as a clear oil: $[\alpha]_D$ +227 (c 0.120, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, J = 8 Hz, 2 H), 7.34−7.26 (m, 7 H), 7.22 (tt, J = 1.5, 7 Hz, 1 H), 6.17 (br s, 1 H), 4.76 (q, J = 6 Hz, 1 H), 4.70 (pent, J = 7 Hz, 1 H), 1.45−1.25 (m, 21 H), 1.09 (d, J = 7 Hz, 3 H), 0.66 (br q, $^1J_{HB}$ = 79 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5 (s, $^4J_{CP}$ = 0.9 Hz), 147.0 (s, $^1J_{CP}$ = 80 Hz), 145.1 (s), 128.7 (d), 128.4 (d), 127.2 (d), 126.4 (d), 126.1 (d), 125.5 (d), 58.3 (d, $^3J_{CP}$ = 12 Hz), 55.1 (d, $^3J_{CP}$ = 8 Hz), 34.0 (s, $^1J_{CP}$ = 18 Hz), 33.8 (s, $^1J_{CP}$ = 19 Hz), 28.5 (q, $^2J_{CP}$ = 2 Hz), 28.4 (q, $^2J_{CP}$ = 2 Hz), 26.9 (C_6H_{12}), 26.7 (q), 26.0 (q); ^{31}P NMR (202 MHz, $CDCl_3$) δ 51.9; HRMS m/z calcd for $C_{25}H_{40}BN_2P$ $[M + H]^+$ 411.3095, found 411.3119.

*(N,N′-(R)-(−)-1-Cyclohexylethylcarbamimidoyl)-di-tert-butylphosphine Borane (**12**).* Prepared according to General Procedure D from **S10** (1.00 g, 3.81 mmol), di-*tert*-butyl phosphine borane (0.731 g, 4.57 mmol, 1.20 equiv), and NaH (0.146 g, 4.57 mmol, 1.20 equiv, 60%) in DMAc (10 mL) and purified by chromatography on SiO_2 (hexanes) to afford **12** (0.571 g, 1.35 mmol, 35%) as a yellow oil that formed a crystalline solid on standing: mp 84 °C; $[\alpha]_D$ −66.3 (c 0.310, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (m, 1 H), 3.49−3.43 (m, 1 H), 3.41−3.34 (m, 1 H), 1.85 (t, J = 15 Hz, 2 H), 1.80−1.62 (m, 8 H), 1.40−1.00 (m, 30 H), 1.06 (d, J = 6.5 Hz, 3 H), 1.02 (d, J = 6.5 Hz, 3 H), 0.52 (br q, J_{HB} = 69 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2 (s, $^1J_{CP}$ = 83 Hz), 58.1 (d, $^3J_{CP}$ = 13 Hz), 55.2 (d, $^3J_{CP}$ = 8 Hz), 45.6 (d), 43.9 (d), 33.9 (s, $^1J_{CP}$ = 27 Hz), 33.3 (s, $^1J_{CP}$ = 27 Hz), 30.1 (t), 29.5 (t), 29.3 (t), 29.0 (t), 28.5 (q, $^2J_{CP}$ = 2 Hz), 28.3 (q, $^2J_{CP}$ = 2 Hz), 26.8 (t), 26.7 (t), 26.6 (t), 26.4 (t), 26.3 (t, $^4J_{CP}$ = 1 Hz), 19.8 (q), 17.9 (q, $^4J_{CP}$ = 1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 49.6 ($^1J_{PB}$ = 46 Hz); HRMS m/z calcd for $C_{25}H_{53}BN_2P$ $[M + H]^+$ 423.4034, found 423.4023.

*(N-Cyclohexyl,N′-phenylcarbamimidoyl)-di(3,5-dimethyl-4-methoxy)phenylphosphine Borane (**13**).* Prepared according to General Procedure D from **S6** (0.070 g, 0.35 mmol), bis-3,5-dimethyl-4-methoxyphenyl phosphine borane (0.132 g, 0.42 mmol, 1.2 equiv), and NaH (0.010 g, 0.42 mmol, 1.2 equiv, 60%) in dimethylacetamide (5 mL) and purified by chromatography on SiO_2 (10% EtOAc/hexanes) to afford **13** (0.153 g, 0.295 mmol, 85%) as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.27 (m, 4 H), 7.05−6.93 (br s, 2 H), 6.82−6.73 (t, 1 H, J = 7.2 Hz), 6.56 (br d, 2 H, J = 7.2 Hz), 5.62−5.50 (m, 1 H), 3.74 (s, 6 H), 3.6−3.4 (br, 1 H), 2.29 (s, 3 H), 2.25 (s, 9 H), 1.90−1.80 (m, 2 H), 1.60−0.85 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (J_{CP} = 3 Hz), 159.9 (J_{CP} = 3 Hz), 158.3, 134.9, 134.7, 134.0, 133.8, 133.6, 133.5, 132.3, 132.2, 131.6, 131.5, 131.44, 131.37, 128.1, 122.0, 121.1, 59.8, 32.7, 25.7, 24.4, 16.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ −37; HRMS m/z calcd for $C_{31}H_{40}N_2O_2P$ $[M + H - BH_3]^+$ 503.2827, found 503.2817.

*(N-Cyclohexyl,N′-phenylcarbamimidoyl)-di-p-tolylphosphine Borane (**14**).* Prepared according to General Procedure D from **S6** (0.160 g, 0.799 mmol), di-tolyl phosphine borane (0.219 g, 0.960 mmol, 1.20 equiv), and NaH (0.038 g, 0.96 mmol, 1.2 equiv, 60%) in DMAc (5 mL) and purified by chromatography on SiO_2 (2% EtOAc/hexanes) to afford **14** (0.175 g, 0.410 mmol, 51%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.50 (br s, 4 H), 7.20 (d, J = 6.8 Hz, 4 H), 7.10−6.96 (br s, 2 H), 6.88−6.80 (br s, 1 H), 6.70−6.51 (br s, 2 H), 5.65−5.48 (br s, 1 H), 3.6−3.1 (br, 1 H), 2.38 (s, 6 H), 1.76−0.80 (m, 13 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 141.8 ($^4J_{CP}$ = 2 Hz), 138.0, 131.0 ($^1J_{CP}$ = 67 Hz), 131.0 ($^3J_{CP}$ = 12 Hz), 129.6, 129.3 ($^3J_{CP}$ = 12 Hz), 124.9, 122.7, 49.4, 33.6, 25.6, 24.9, 21.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ −38; HRMS m/z calcd for $C_{27}H_{32}N_2P$ $[M + H - BH_3]^+$ 415.2303, found 415.2298.

*(N,N′-(R)-(+)-Methylbenzylcarbamimidoyl)-di(3,5-methyl-4-methoxy)phenylphosphine Borane (**15**).* Prepared according to General Procedure D from **S9** (0.210 g, 0.840 mmol), di-3,5-dimethyl-4-methoxyphenyl phosphine borane (0.279 g, 0.882 mmol, 1.20 equiv), and NaH (0.212 g, 0.882 mmol, 1.20 equiv, 60%) in DMAc (3 mL) and purified by chromatography on SiO_2 (15% EtOAc/hexanes) to afford **15** (0.218 g, 0.384 mmol, 44%, adjusted for residual solvent) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.26 (m, 5 H), 7.14 (d, 2 H, J = 10.8 Hz), 7.09 (d, 2 H, J = 11.2 Hz), 6.96−6.86 (m, 3 H), 6.48 (d, J = 7.2 Hz, 2 H), 5.12 (p, J = 6.6 Hz, 1 H), 4.89 (d, J = 4.0 Hz, 1 H), 4.62 (q, J = 6.2 Hz, 1 H), 3.70 (s, 3 H), 3.65 (s, 3 H), 2.16 (s, 6 H), 2.05 (s, 6 H), 1.4−0.9 (m, 3 H), 1.36 (d, J = 6.8 Hz, 3 H), 1.13 (d, J = 6.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 ($^4J_{CP}$ = 3 Hz), 159.7 ($^4J_{CP}$ = 3 Hz), 146.1 ($^1J_{CP}$ = 92 Hz), 144.4 ($^1J_{CP}$ = 32 Hz), 133.8, 133.7, 133.2, 133.1, 132.2, 132.1 ($^3J_{CP}$ = 12 Hz), 128.3, 127.3, 126.7, 126.0, 125.7, 125.4, 121.8, 121.3, 121.0, 120.4, 60.4, 59.7, 59.4, 59.3, 51.8, 51.7, 26.7, 23.0, 21.0, 16.1, 15.9, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.0 (s); ^{11}B NMR (128 MHz, $CDCl_3$) δ −36; HRMS m/z calcd for $C_{35}H_{42}N_2O_2P$ $[M + H - BH_3]^+$ 553.2984, found 553.2980.

*(R_P,1R,2S,5R)-Menthyl)phenylphosphinite Borane (**16**).*[8] A four-neck 3 L flask equipped with a graduated 1 L addition funnel, inert gas valve, and septum with thermocouple was charged with menthol (176 g, 1.13 mol). The flask was then twice backfilled with Ar, and anhydrous THF (1.00 L) was charged via canula under N_2 pressure. An endotherm to 6 °C was observed. The resulting colorless solution was cooled to 2 °C in an ice bath, and *n*-BuLi (683 mL, 1.64 M, 1.12 mol, 0.99 equiv) was then charged to the addition funnel and added dropwise to the cold menthol solution. It was necessary to stop the addition several times and allow the internal temperature to fall again to ∼6 °C before resuming the addition. The entire addition required 1.5 h, and the internal temperature rose to a maximum of 14 °C.

A separate four-neck 5 L flask equipped with a mechanical stirrer, inert gas valve, and septa with a thermocouple was charged with $PhPCl_2$ (152.0 mL, 1.120 mol, 1.000 equiv). The flask was then evacuated and backfilled with Ar, and MTBE (0.500 L) was charged via cannula under N_2 pressure. The resulting solution was cooled to −78 °C under Ar. The cold (∼3 °C) menthoxide solution from above

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was transferred via cannula under N_2 pressure to the MTBE solution over 1.5 h while maintaining an internal temperature below −50 °C. The cold bath was removed, and the reaction mixture was stirred at room temperature for 1.5 h, giving a nearly colorless fine slurry. This mixture was cooled again to −78 °C, and 95% $LiBH_4$ (29.3 g, 1.34 mol, 1.2 equiv, weighed in a glovebox) was added at once by quickly removing a septum while flowing an external source of N_2 through the flask. An exotherm to −45 °C was observed. The external N_2 source was removed, and the reaction mixture was warmed to room temperature overnight.

A separate three-neck 5 L flask equipped with a mechanical stirrer was charged with ice (500 g), H_2O (500 mL), and conc. HCl (230 mL). The reaction mixture from above was slowly added in small portions over 30 min. The resulting mixture was stirred for 15 min and then poured into a 5 L separatory funnel, and the phases were separated. The lower, aqueous layer was then extracted with MTBE (2 × 1 L). The solvents from the combined organic extracts were removed under reduced pressure, giving a viscous, nearly colorless oil. This oil was then washed through a wide column of 750 g of SiO_2 that had been prewetted with hexanes:MTBE (1:1). The product containing fractions were combined, and the solvents were removed in vacuo to give a viscous oil (175 g). A seed crystal of the product phosphinite borane was added, causing a slow crystallization of the batch, which, upon filtration, afforded **16** (88.0 g, 28% overall yield) as a colorless, crystalline solid 52:48 R_P:S_P mixture of diastereomers. A portion of this solid (20.0 g) was recrystallized twice (hexanes), ultimately affording **16** (3.50 g, 12.6 mmol, ca. 5% overall yield, >15:1 R_P:S_P) as colorless needles: mp 96 °C; $[\alpha]_D$ −113.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81−7.76 (m, 2 H), 7.59−7.56 (m, 1 H), 7.53−7.48 (m, 2 H), 7.16 (dq, $^1J_{HP}$ = 396 Hz, $^2J_{HB}$ = 5.7 Hz, 1 H), 3.89 (dq, 1 H, *J* = 10 Hz, 4 Hz), 2.07−2.01 (m, 2 H), 1.65−1.49 (m, 2 H), 1.41−1.35 (m, 2 H), 1.24−0.68 (m, 6 H), 0.88 (d, *J* = 6 Hz, 6 H), 0.63 (d, *J* = 7 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.6 (d, $^2J_{CP}$ = 2.3 Hz), 132.1 (d), 132.0 (d), 129.5 (s, $^1J_{CP}$ = 63 Hz), 128.9 (d), 128.8 (d), 80.1 (d, $^2J_{CP}$ = 7 Hz), 48.8 (d, $^3J_{CP}$ = 5 Hz), 42.3 (t, J_{CP} = 1.5 Hz), 34.0 (t), 31.5 (d, J_{CP} = 3 Hz), 25.6 (d), 23.0 (t), 22.0 (q), 20.9 (q), 15.8 (q); ^{31}P NMR (202 MHz, $CDCl_3$) δ 91.9 ($^1J_{PH}$ = 389 Hz, $^1J_{PB}$ = 63 Hz).

General Procedure E: Preparation of Phosphinite Boranes. *(1R,2S,5R-Menthyl)(N,N′-(R)-(+)-methylbenzylcarbamimidoyl)-phenylphosphinite Borane (**17**).* A 15 mL three-neck, round-bottom flask equipped with a direct Ar line, inert gas valve, and septum with thermocouple was charged with **16** (0.300 g 1.05 mmol, 1 equiv), **S9** (0.319 g, 1.26 mmol, 1.2 equiv), and dry THF (3.0 mL). The solution was sparged with Ar for 15 min and cooled to −78 °C, and *n*-BuLi (0.66 mL, 1.05 mmol, 1 equiv, 1.6 M in hexane) was added dropwise via syringe, giving a yellow reaction mixture. The cold bath was removed, and the mixture was allowed to warm to rt for 30 min. The reaction mixture was applied directly to a silica gel cartridge (40 g) and purified by chromatography on SiO_2 (20:1, hexanes:EtOAc) to afford **17** (0.290 g, 0.549 mmol, 52%) as a clear, colorless oil: $[\alpha]_D$ −2.5 (*c* 0.028, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.60 (m, 2 H), 7.39−7.24 (m, 10 H), 6.94−6.86 (m, 3 H), 6.55 (d, *J* = 7 Hz, 2 H), 5.87 (d, *J* = 5 Hz, 1 H), 5.14 (pent, *J* = 7 Hz, 1 H), 4.70 (q, *J* = 6 Hz, 1 H), 4.35−4.25 (m, 1 H), 1.79−1.72 (m, 2 H), 1.59−1.54 (m, 4 H), 1.56 (d, *J* = 7 Hz, 3 H), 1.27−0.61 (m, 3 H), 0.98 (d, *J* = 6 Hz, 3 H), 0.95−0.85 (m, 3 H), 0.77 (t, *J* = 6 Hz, 6 H), 0.58 (d, *J* = 7 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9 (s, $^1J_{CP}$ = 46 Hz), 146.6 (s, $^4J_{CP}$ = 0.8 Hz), 145.2 (s), 143.7 (s), 132.6 (s, $^1J_{CP}$ = 58 Hz), 131.8 (s, $^4J_{CP}$ = 3 Hz), 130.6 (d), 130.5 (d), 128.63 (d), 128.54 (d), 128.4 (d), 127.3 (d), 126.7 (d), 126.3 (d), 126.0 (d), 125.7 (d), 125.4 (d), 81.2 (d, $^2J_{CP}$ = 5 Hz), 57.6 (d, $^3J_{CP}$ = 14 Hz), 51.2 (d, J_{CP} = 5 Hz), 48.7 (d, $^3J_{CP}$ = 58 Hz), 43.4 (t, J_{CP} = 0.5 Hz), 33.9 (t), 31.4 (d), 26.9 (t, C_6H_{12}), 26.2 (q), 25.8 (d), 24.6 (q), 22.60 (d), 22.57 (t), 22.0 (q), 20.8 (q), 15.6 (q); ^{31}P NMR (202 MHz, $CDCl_3$) δ 96.1; HRMS *m*/*z* calcd for $C_{33}H_{47}BN_2OP$ $[M + H]^+$ 529.3514, found 529.3535.

*(1R,2S,5R-Menthyl)(N,N′-dicyclohexylcarbamimidoyl)phenylphosphinite Borane (**18**).* Prepared according to General Procedure E from **16** (0.080 g, 0.29 mmol, 1.2 equiv), DCC (0.050 g, 0.24 mmol, 1.0 equiv), and *n*-BuLi (0.18 mL, 0.29 mmol, 1.6 M in hexane, 1.2 equiv) in THF (6 mL) and purified by chromatography on SiO_2 (15% EtOAc/hexanes) to afford **18** (0.024 g, 0.050 mmol, 20% accounting for solvent impurity) as a sticky clear oil: $[\alpha]_D$ −9.8 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82−7.77 (m, 2 H), 7.52−7.42 (m, 3 H), 5.35 (br s, 1 H), 4.39−4.31 (m, 1 H), 3.90−3.71 (m, 1 H), 3.40−3.32 (m, 1 H), 2.11−2.03 (m, 3 H), 1.80−0.60 (m, 38 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 134.2, 133.7, 131.9, 131.0, 130.8, 128.6, 128.5, 80.6 ($^2J_{CP}$ = 6 Hz), 57.9 (J_{CP} = 17 Hz), 49.1 (J_{CP} = 6 Hz), 43.3, 34.5, 34.0, 33.9, 32.3, 32.2, 31.4, 26.1, 26.0, 25.6, 24.8, 24.6, 24.5, 22.7, 21.9, 21.1, 15.8; ^{31}P NMR (202 MHz, $CDCl_3$) δ 94.0; ^{11}B NMR (160 MHz, $CDCl_3$) δ −39.5; HRMS *m*/*z* calcd for $C_{29}H_{48}N_2OP$ $[M + H - BH_3]^+$ 471.3504, found 471.3498.

General Procedure F: Deprotection of Phosphine Boranes to Afford Phosphine Oxides. *(N-Cyclohexyl,N′-phenylcarbamimidoyl)-di(3,5-dimethyl-4-methoxy)phenylphosphine (**19**).* A solution of **13** (0.095 g, 0.18 mmol) in toluene (3 mL) was treated with DABCO (0.404 g, 0.736 mmol, 4.00 equiv) and stirred at 65 °C for 1.5 h under N_2. The reaction mixture was directly added on top of a SiO_2 column and purified by chromatography on SiO_2 (10% EtOAc/hexanes) to afford **19** (0.067 g, 0.13 mmol, 72%) as a colorless sticky oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06−7.01 (m, 6 H), 6.86 (t, *J* = 7.2 Hz, 1 H), 6.64 (d, *J* = 7.6 Hz, 1 H), 4.42 (d, *J* = 7.2 Hz, 1 H), 4.01 (br s, 1 H), 3.75 (s, 6 H), 2.27 (s, 12 H), 1.92 (br d, 2 H, *J* = 8.0 Hz), 1.52−1.11 (m, 9 H), 1.00−0.88 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 157.9 ($^1J_{CP}$ = 37 Hz), 151.3 ($^3J_{CP}$ = 12 Hz), 134.8 ($^2J_{CP}$ = 21 Hz), 131.4 ($^3J_{CP}$ = 8 Hz), 129.1, 129.0, 128.0, 123.1, 121.8, 59.8, 49.0, 32.3, 25.9, 24.1, 16.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ −15.5; HRMS *m*/*z* calcd for $C_{31}H_{40}N_2O_2P$ $[M + H]^+$ 503.2827, found 503.2826.

*(N-Cyclohexyl,N′-phenylcarbamimidoyl)-di-p-tolylphosphine (**20**).* Prepared according to General Procedure F from **14** (0.122 g, 0.285 mmol) and DABCO (0.132 g, 1.14 mmol, 4.00 equiv) in toluene (5 mL) and purified by chromatography on SiO_2 (10% EtOAc/hexanes) to afford **20** (0.094 g, 0.23 mmol, 80%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.0 Hz, 4 H), 7.15 (d, *J* = 8.0 Hz, 4 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.85 (br s, 1 H), 6.65 (br s, 2 H), 4.35−4.23 (br s, 1 H), 4.02−3.89 (br s, 1 H), 2.36 (s, 6 H), 2.00−1.90 (m, 2 H), 1.53−1.51 (m, 3 H), 1.38−1.36 (m, 2 H), 1.18−1.13 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2 ($^1J_{CP}$ = 46 Hz), 149.8 ($^1J_{CP}$ = 67 Hz), 142.4, 132.2 ($^3J_{CP}$ = 9 Hz), 129.1 ($^3J_{CP}$ = 13 Hz), 128.6, 128.3, 127.5, 122.0, 120.6, 51.6, 33.4, 25.3, 24.7, 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ −16.2 (s); HRMS *m*/*z* calcd for $C_{27}H_{32}N_2P$ $[M + H]^+$ 415.2303, found 415.2298.

*(N,N′-Dicyclohexylcarbamimidoylium)-dicyclohexylphosphine Borane Tetrafluoroborate (**21**).* A solution of phosphine borane **1** (0.077 g, 0.18 mmol) in CH_2Cl_2 (1.5 mL) was cooled to 0 °C under Ar and treated with HBF_4 diethyl ether complex (0.37 mL, 2.8 mmol, 15 equiv). After 30 min at 0 °C, the reaction mixture was warmed to rt over 30 min. The solution was then left open to air, treated with an equal volume of HBF_4 (conc. aq.), and stirred for 30 min more. The solution was then diluted with water (5 mL) and extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to afford **21** (0.075 g, 0.15 mmol, 81%) as a colorless crystalline solid: mp 259−261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.34 (br s, 1 H), 4.75−4.65 (m, 1 H), 3.62−3.38 (m, 2 H), 2.40−2.25 (m, 2 H), 1.95−1.10 (m, 38 H), 0.9−0.1 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ 158.1 ($^1J_{CP}$ = 30 Hz), 156.2 ($^1J_{CP}$ = 27 Hz), 58.6, 53.3 ($^3J_{CP}$ = 3 Hz), 34.9, 34.7, 32.8, 32.6, 32.1, 31.8, 31.2, 28.3, 27.8, 27.7, 27.2, 26.42, 26.38, 26.3, 26.0, 25.9, 25.8, 25.7, 25.42, 25.40, 25.1, 25.0, 24.4, 24.2, 23.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 60.0, 56.9; ^{11}B NMR (128 MHz, $CDCl_3$, measured without lock) δ −0.9, −45.4. These spectra exhibit a mixture of E_{syn} + Z_{syn} conformers. A single crystal suitable for X-ray analysis was grown from hexanes/acetone (1:1). The X-ray crystal structure data for the compound has been deposited, with CCDC No. 997593.

*N-Cyclohexyl,N′-phenylcarbamimidoyl)-di(3,5-dimethyl-4-methoxyphenyl)phosphine Oxide (**22**).* A solution of phosphine **19** (0.052 g, 0.10 mmol) in acetone (1 mL) was treated with hydrogen peroxide (0.12 mL, 0.11 mmol, 3% aq. solution). The reaction mixture was stirred for 1 h at rt; TLC analysis (10% EtOAc/hexanes) showed a

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clean and quantitative oxidation. The solution was extracted with Et_2O (2 × 10 mL). The combined organic extracts were washed with water (10 mL) and brine (10 mL), dried (Na_2SO_4), and concentrated to afford phosphine oxide **22** (0.053 g, 0.10 mmol, 99%) as a sticky colorless gum: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.41 (m, 3 H), 7.22−6.60 (m, 5 H), 6.30−6.20 (br s, 1 H), 3.74 (s, 6 H), 2.28 (s, 12 H), 1.78−0.95 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (s), 132.9, 132.8, 131.3, 131.2, 128.2, 126.3, 125.3, 122.0, 120.8, 59.6, 33.3, 25.4, 24.7, 16.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.0; HRMS *m*/*z* calcd for $C_{31}H_{40}N_2O_3P$ $[M + H]^+$ 519.2777, found 519.2764.

*5,6-Didehydro-12,13-dihydro-5H-dibenzo[d,h][1,3]diazonine (**23**).*[13] A solution of dianiline (3.50 g, 16.4 mmol) in 2 M HCl (60 mL) was cooled to 0 °C and treated dropwise with a solution of sodium nitrite (4.60 g, 66.8 mmol) in H_2O (30 mL). The reaction mixture turned yellow and was left to stir for 1 h at 0 °C and then was treated dropwise with a solution of sodium azide (4.45 g, 68.4 mmol) in H_2O (35 mL). The mixture was allowed to warm to rt for 14 h, and a tan precipitate formed. After addition of CH_2Cl_2 (75 mL) and H_2O (10 mL), the organic layer was dried (Na_2SO_4) and concentrated in vacuo to afford the bis-azide (2.86 g, 10.8 mmol, 66%) as a tan solid that was used without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35- 7.04 (m, 8 H), 2.85 (s, 4 H); IR (ATR) 3085, 2993, 2115, 1485, 1286, 1163, 751 cm^{-1}.

A solution of bis-azide (0.749 g, 2.83 mmol) in ether (10 mL) was treated at rt with triphenylphosphine (1.49 g, 5.67 mmol). The opaque reaction mixture was stirred at rt for 14 h and concentrated to afford the bis-iminophosphorane (1.852 g, 2.52 mmol, 89%) as a brown solid that was used without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.23 (m, 32 H), 7.12−7.01 (d, 3 H, *J* = 6.6 Hz), 6.80−6.45 (m, 6 H), 3.23−3.05 (s, 4 H); IR (ATR) 3026, 1594, 1479, 1450, 1340, 1103, 726, 691 cm^{-1}.

A suspension of bis-iminophosphorane (7.55 g, 10.3 mmol) in CH_2Cl_2 (300 mL) was treated at rt with Boc-anhydride (4.49 g, 20.6 mmol) and DMAP (1.26 g, 10.3 mmol). The reaction mixture was allowed to stir for 12 h under N_2 and became a transparent brown solution. Evaporation of the solvent led to a dark residue that was purified by chromatography on SiO_2 (15% EtOAc/hexanes) to provide a crude product that was recrystallized (hexanes) to afford carbodiimide **23** (1.17 g, 2.27 mmol, 52%) as a brown flaky solid: mp 141.9−142.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.20 (m, 4 H), 7.16−7.01 (m, 4 H), 3.41−3.27 (m, 2 H), 3.12−2.97 (m, 2 H); IR (ATR) 2974, 2104, 2091, 1737, 1595, 1450, 1140, 734 cm^{-1}. This material contained ca. 10% of dimeric bis-carbodiimide that was readily removed in subsequent tranformations.

*6-(Di-tert-butylphosphanyl)-12,13-dihydro-5H-dibenzo[d,h][1,3]-diazonine Borane (**24**).* A solution of carbodiimide **23** (0.065 g, 0.30 mmol) and di-*t*-butyl phosphine borane (0.057 g, 0.35 mmol) in DMAc (1.2 mL) was sparged with Ar for 10 min, cooled to 0 °C, and treated with NaH (0.014 g, 0.35 mmol, 60% dispersion). The reaction mixture was stirred for 10 min at 0 °C, warmed to rt over 20 min, exposed to air, stirred for 30 min, and quenched with sat. aq. NH_4Cl. The mixture was extracted with diethyl ether (3 × 30 mL), and the combined organic extracts were washed with H_2O (50 mL) and brine (50 mL), dried (Na_2SO_4), and concentrated to provide a crude residue that was purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford **24** (0.075 g, 0.20 mmol, 67%) as a colorless crystalline solid: mp 174−177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1 H), 6.92−6.73 (m, 5 H), 6.69 (d, 1 H, *J* = 7.2 Hz), 6.63 (t, 1 H, *J* = 7.2 Hz), 6.49 (d, 1 H, *J* = 7.6 Hz), 3.45−3.26 (m, 2 H), 2.97−2.83 (m, 2 H), 1.58 (s, 9 H), 1.54 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9 ($^3J_{CP}$ = 11 Hz), 146.3 ($^1J_{CP}$ = 75 Hz), 137.7, 137.5 ($^3J_{CP}$ = 8 Hz), 130.9, 130.2, 128.4, 127.0, 126.7, 126.6, 126.5, 122.3, 120.3, 34.3 ($^1J_{CP}$ = 27 Hz), 33.6 ($^1J_{CP}$ = 26 Hz), 30.4 ($^2J_{CP}$ = 7 Hz), 28.8, 28.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ −42; HRMS *m*/*z* calcd for $C_{23}H_{34}N_2PB$ $[M + H]^+$ 381.2631, found 381.2622. The X-ray crystal structure data for this compound have been deposited (CCDC No. 1008171).

*6-(Di-tolylphosphanyl)-12,13-dihydro-5H-dibenzo[d,h][1,3]-diazonine Borane (**25**).* A solution of carbodiimide **23** (0.200 g, 0.907 mmol) and di-tolyl phosphine borane (0.249 g, 1.09 mmol) in DMAc (5 mL) was sparged with Ar for 10 min and then cooled to 0 °C and treated with NaH (0.022 g, 0.54 mmol, 60% dispersion). The reaction mixture turned yellow and was stirred for 20 min at 0 °C, warmed to rt for 20 min, exposed to air, quenched with sat. aq. NH_4Cl solution, and extracted with diethyl ether (3 × 30 mL). The combined organic extracts were washed with H_2O (50 mL) and brine (50 mL), dried (Na_2SO_4), and concentrated to give a crude residue that was purified by chromatography on SiO_2 (10% EtOAc/hexanes) to afford phosphine borane **25** (0.319 g, 0.712 mmol, 78%) as a colorless crystalline solid: mp 189.7−191.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 1 H, *J* = 8.0 Hz), 7.98 (d, 1 H, *J* = 8.4 Hz), 7.85 (d, 1 H, *J* = 8.0 Hz), 7.82 (d, 1 H, *J* = 8.4 Hz), 7.42 (s, 1 H), 7.31 (td, 4 H, *J* = 6.4, 2.0 Hz), 6.86−6.80 (m, 3 H), 6.79−6.72 (m, 2 H), 6.63−6.54 (m, 2 H), 6.42 (d, 1 H, *J* = 7.6 Hz), 3.23−3.15 (m, 1 H), 2.97−2.86 (m, 1 H), 2.78−2.66 (m, 2 H), 2.43 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7 ($^1J_{CP}$ = 91 Hz), 148.0 ($^3J_{CP}$ = 13 Hz), 142.7 ($^4J_{CP}$ = 2 Hz), 142.1 ($^4J_{CP}$ = 2 Hz), 137.3 ($^3J_{CP}$ = 10 Hz), 136.9, 133.6 ($^2J_{CP}$ = 10 Hz), 133.2 ($^2J_{CP}$ = 10 Hz), 130.7, 130.4, 129.6 ($^3J_{CP}$ = 11 Hz), 128.4, 126.6, 126.5, 125.4, 124.2 ($^1J_{CP}$ = 64 Hz), 123.3 ($^1J_{CP}$ = 61 Hz), 122.6, 119.6, 31.1, 29.2, 21.7, 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ −40.4; IR (ATR) 3340, 3026, 2378, 1637, 1486, 1356, 1128, 1045, 908, 802, 734 cm-1; HRMS *m*/*z* calcd for $C_{29}H_{28}N_2P$ $[M + H - BH_3]^+$ 435.1990, found 435.1975.

*6-(Di-(3,5-dimethyl-4-methoxy)phenylphosphanyl)-12,13-dihydro-5H-dibenzo[d,h][1,3]diazonine Borane (**26**).* A solution of carbodiimide **23** (0.084 g, 0.38 mmol) and di-(3,5-dimethyl-4-methoxy)phosphine borane (0.133 g, 0.545 mmol) in DMAc (3 mL) was sparged with Ar for 10 min, cooled to 0 °C, and treated with NaH (0.018 g, 0.458 mmol, 60% dispersion). The reaction mixture turned yellow and was stirred for 20 min at 0 °C, warmed to rt for 20 min, exposed to air for 30 min, quenched with sat. aq. NH_4Cl (3 mL), and extracted with diethyl ether (3 × 30 mL). The combined organic extracts were washed with H_2O (50 mL) and brine (50 mL), dried (Na_2SO_4), and concentrated to give a crude residue that was purified by chromatography on SiO_2 (10% EtOAc/hexanes) to afford phosphine borane **26** (0.176 g, 0.328 mmol, 86%) as a colorless foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2 H, *J* = 10.8 Hz), 7.54 (d, 2 H, *J* = 11.2 Hz), 7.43 (s, 1 H), 6.89−6.83 (m, 3 H), 6.80−6.74 (m, 2 H), 6.63−6.55 (m, 2 H), 6.44 (d, 1 H, *J* = 7.6 Hz), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.27−3.18 (m, 1 H), 2.92−2.81 (m, 1 H), 2.79−2.68 (m, 2 H), 2.36 (s, 6 H), 2.33 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5 ($^4J_{CP}$ = 2 Hz), 159.9 ($^4J_{CP}$ = 2 Hz), 149.2 ($^1J_{CP}$ = 91 Hz), 148.0 ($^3J_{CP}$ = 13 Hz), 137.3 ($^3J_{CP}$ = 10 Hz), 136.6, 134.3 ($^2J_{CP}$ = 11 Hz), 133.8 ($^2J_{CP}$ = 10 Hz), 131.8 ($^3J_{CP}$ = 24 Hz), 131.8, 130.6 ($^3J_{CP}$ = 17 Hz), 128.4, 126.7, 126.5, 126.4, 125.1, 122.6, 122.0 ($^1J_{CP}$ = 65 Hz), 120.9 ($^1J_{CP}$ = 60 Hz), 119.4, 59.8, 59.7, 31.2, 28.8, 16.4, 16.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ −38.3; IR (ATR) 3345, 2934, 2378, 1637, 1480, 1278, 1114, 917, 734 cm^{-1}; HRMS *m*/*z* calcd for $C_{33}H_{36}N_2O_2P$ $[M + H - BH_3]^+$ 523.2514, found 523.2494.

*6-(Cyclohexylphenylphosphanyl)-12,13-dihydro-5H-dibenzo-[d,h][1,3]diazonine Borane (**27**).* A solution of carbodiimide **23** (0.100 g, 0.454 mmol) and phenylcyclohexyl phosphine borane (0.112 g, 0.545 mmol) in DMAc (2 mL) was sparged with Ar for 10 min, cooled to 0 °C, and treated with NaH (0.022 g, 0.55 mmol, 60% dispersion). The reaction mixture turned yellow and was stirred for 20 min at 0 °C, warmed to rt for 20 min, exposed to air for 30 min, quenched with sat. aq. NH_4Cl (2 mL) solution, and extracted with diethyl ether (3 × 30 mL). The combined organic extracts were washed with H_2O (50 mL) and brine (50 mL), dried (Na_2SO_4), and concentrated to give a crude residue that was purified by chromatography on SiO_2 (hexanes) to afford phosphine borane **27** (0.134 g, 0.314 mmol, 69%) as a colorless solid that exists as an equilibrating mixture of diastereomers in solution: mp 164−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18−8.09 (m, 2 H), 7.63−7.48 (m, 3 H), 7.28 (s, 0.7 H), 7.13 (s, 0.3 H), 6.93−6.74 (m, 4 H), 6.69 (d, 1 H, *J* = 7.6 Hz), 6.65−6.54 (m, 2 H), 6.49 (d, 1 H, *J* = 7.6 Hz), 3.20−3.09 (m, 0.5 H), 3.10 (dd, 1 H, *J* = 9.6, 2.4 Hz), 3.04−2.71 (m, 1.5 H), 2.69−2.60 (m, 1 H), 2.58−2.43 (m, 1.5 Hz), 2.30−2.15 (m, 1 H), 1.97−1.86 (m, 1 H), 1.80−1.65 (m, 3 H), 1.48−1.17 (m, 6 H), 1.1−

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0.4 (br, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 148.0, 147.4 ($^1J_{CP}$ = 57 Hz), 137.2, 137.1, 133.0, 132.9, 132.1, 130.7, 130.5, 130.4, 128.8, 128.7, 128.7, 128.6, 128.5, 127.1, 126.8, 126.5, 126.4, 126.3, 125.5, 124.9, 122.6, 119.9, 119.8, 33.5, 33.2, 33.1, 31.1, 30.7, 30.2, 28.4, 26.7, 26.5, 26.4, 25.9, 25.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.1, 25.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ −44.3; IR (ATR) 3353, 2934, 2385, 1644, 1474, 1435, 1260, 726, 692 cm^{-1}; HRMS *m*/*z* calcd for $C_{27}H_{33}N_2PB$ $[M + H]^+$ 427.2474, found 427.2466.

*6-(Di-tolylphosphanyl)-12,13-dihydro-5H-dibenzo[d,h][1,3]diazonine (**28**).* A solution of phosphine borane **25** (0.071 g, 0.16 mmol) in toluene (2 mL) was treated under an Ar atmosphere with DABCO (0.025 g, 0.22 mmol) and stirred at 60 °C for 90 min. After cooling to rt, the reaction mixture was purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford phosphine **28** (0.056 g, 0.13 mmol, 81%) as sticky clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.48 (m, 4 H), 7.25−7.19 (m, 2 H), 6.88−6.76 (m, 2 H), 6.76−6.59 (m, 3 H), 6.54 (d, 2 H, *J* = 7.6 Hz), 3.38 (d, 2 H, *J* = 8.8 Hz), 2.83 (d, 2 H, *J* = 9.2 Hz), 2.38 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 139.9, 134.3 (d, $^3J_{CP}$ = 19 Hz), 131.3 (d, $^3J_{CP}$ = 11 Hz), 130.4, 129.9, 129.8, 126.3, 30.5, 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −3.7; HRMS *m*/*z* calcd for $C_{29}H_{28}N_2P$ $[M + H]^+$ 435.1990, found 435.1991.

*6-(Di-(3,5-dimethyl-4-methoxy)phenylphosphanyl)-12,13-dihydro-5H-dibenzo[d,h][1,3]diazonine (**29**).* A solution of phosphine borane **26** (0.176 g, 0.328 mmol) in toluene (2 mL) was treated under an Ar atmosphere with DABCO (0.147 g, 1.31 mmol) and stirred at 60 °C for 90 min. After cooling to rt, the reaction mixture was purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford phosphine **29** (0.112 g, 0.214 mmol, 65%) as a sticky oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.29 (br m, 4 H), 6.89−6.50 (br m, 8 H), 6.25−6.10 (br s, 1 H), 3.80 (s, 6 H), 3.65−3.15 (br m, 2 H), 3.00−2.68 (br m, 2 H), 2.35 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 156.7, 156.6, 135.2, 135.0, 131.7, 130.5, 129.5, 129.4, 126.3, 59.7, 31.4, 29.5, 16.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ −3.2; HRMS *m*/*z* calcd for $C_{33}H_{36}N_2O_2P$ $[M + H]^+$ 523.2514, found 523.2494.

*6-(Cyclohexylphenylphosphanyl)-12,13-dihydro-5H-dibenzo-[d,h][1,3]diazonine (**30**).* A solution of phosphine borane **27** (0.099 g, 0.23 mmol) in toluene (2 mL) was treated under an Ar atmosphere with DABCO (0.104 g, 0.929 mmol) and heated at 60 °C for 90 min. After cooling, the reaction mixture was purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford phosphine **30** (0.090 g, 0.22 mmol, 94%) as a colorless oil that forms an equilibrating mixture of diastereomers in solution: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.75 (m, 2 H), 7.51−7.38 (m, 3 H), 6.94−6.73 (m, 4 H), 6.74−6.63 (m, 2 H), 6.63−6.51 (m, 2 H), 6.51−6.43 (m, 2 H), 6.03−6.08 (s, 0.3 H), 3.52−3.23 (m, 1.5 H), 3.04−2.57 (m, 2.5 H), 2.49 (d, 1 H, *J* = 7.6 Hz), 2.39−2.24 (m, 1 H), 1.95−1.28 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 149.5, 138.6, 136.4, 135.1, 135.0, 134.7, 134.6, 133.9, 133.8, 130.6, 130.4, 130.1, 128.8, 128.4, 126.6, 126.4, 126.1, 125.5, 125.1, 124.1, 121.7, 120.3, 119.6, 35.8, 34.8, 31.6, 31.1, 30.7, 30.2, 29.9, 29.8, 28.6, 28.2, 27.7, 27.6, 26.8, 26.5, 26.3, 26.1, 25.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.6, 2.5; HRMS *m*/*z* calcd for $C_{27}H_{30}N_2P$ $[M + H]^+$ 413.2147, found 413.2144.

*6-(Di-(3,5-dimethyl-4-methoxy)phenylphosphanyloxide)-12,13-dihydro-5H-dibenzo[d,h][1,3]diazonine (**31**).* A solution of phosphine **29** (0.094 g, 0.18 mmol) in acetone (1 mL) was treated with hydrogen peroxide (0.2 mL, 0.2 mmol, 3% aq. solution) at rt. After stirring for 15 min, the reaction mixture was partitioned between water (20 mL) and EtOAc (20 mL). The phases were separated, and the aqueous phase was re-extracted with EtOAc (20 mL). The combined organic layers were washed with water (25 mL) and brine (25 mL), dried (Na_2SO_4), and concentrated to afford phosphine oxide **31** (0.088 g, 0.16 mmol, 91%) as a colorless crystalline solid: mp 236−238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, 1 H, *J* = 2.8 Hz), 7.81 (d, 2 H, *J* = 12.0 Hz), 7.76 (d, 2 H, *J* = 12.0 Hz), 6.89−6.73 (m, 5 H), 6.66−6.56 (m, 2 H), 6.43 (d, 1 H, *J* = 7.6 Hz), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.21−3.09 (m, 1 H), 2.98−2.87 (m, 1 H), 2.81−2.66 (m, 2 H), 2.34 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 160.6, 160.5, 160.5, 150.6, 149.1, 147.8, 147.6, 137.1, 137.0, 136.7, 133.1, 133.0, 132.8, 132.6, 131.6, 131.5, 131.5, 131.4, 130.7, 130.4, 128.7, 126.7, 126.5, 126.5, 126.1, 125.9, 125.6, 125.0, 124.9, 122.6, 119.9, 59.7, 59.7, 31.0, 29.0, 16.3, 16.2; ^{31}P NMR (162 MHz, $CDCl_3$) 18.5; IR (ATR) 3202, 2934, 1627, 1480, 1286, 1215, 1163, 1115, 994, 758 cm^{-1}; HRMS *m*/*z* calcd for $C_{33}H_{36}N_2PO_3$ $[M + H]^+$ 539.2464, found 539.2443.

■ ASSOCIATED CONTENT

Supporting Information

Spectral data for all new compounds as well as CIF files and ORTEP plots for compounds **4**, **5**, **21**, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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